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Batterie secondaire

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(56) References cited:

EP-A- 0 486 704 **DE-A- 2 834 485**
US-A- 3 653 972 **US-A- 4 184 017**
US-A- 5 116 701

- **PATENT ABSTRACTS OF JAPAN** vol. 16 no. 499
(E-1280), 15 October 1992 & JP-A-04 184870
(**MITSUBISHI PETROCHEM CO LTD**)
- **PATENT ABSTRACTS OF JAPAN** vol. 16 no. 73
(E-1169), 21 February 1992 & JP-A-03 263758
(**ASAHI CHEM IND CO LTD**)
- **PATENT ABSTRACTS OF JAPAN** vol. 4 no. 178
(C-034), 10 December 1980 & JP-A-55 118988
(**MATSUMOTO YUSHI SEIYAKU KK**)
- **PATENT ABSTRACTS OF JAPAN** vol. 14 no. 564
(E-1013), 14 December 1990 & JP-A-02 244565
(**ASAHI CHEM IND CO LTD**)
- **PATENT ABSTRACTS OF JAPAN** vol. 14 no. 38
(E-878), 24 January 1990 & JP-A-01 272053
(**HITACHI MAXELL LTD**)
- **PATENT ABSTRACTS OF JAPAN** vol. 17 no. 535
(E-1439), 27 September 1993 & JP-A-05 151971
(**FUJI ELECTROCHEM CO LTD**)
- **PATENT ABSTRACTS OF JAPAN** vol. 12 no. 320
(E-651), 30 August 1988 & JP-A-63 086355 (**FUJI
ELECTROCHEM CO LTD**)
- **PATENT ABSTRACTS OF JAPAN** vol. 13 no. 92
(E-722), 3 March 1989 & JP-A-63 269461 (**SANYO
ELECTRIC CO LTD**)
- **PATENT ABSTRACTS OF JAPAN** vol. 13 no. 433
(E-824), 27 September 1989 & JP-A-01 161671
(**SANYO ELECTRIC CO LTD**)

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Description**Field of the Invention**

- 5 [0001] The present invention relates to batteries with high safety, and more particularly to secondary batteries maintaining high safety even after repeated uses and having higher energy density.

Related Background Art

- 10 [0002] Recently, it is foreseen that the earth will be increasingly warmer due to greenhouse effect with the increase of CO₂, which makes it difficult to construct new thermal power plants, and thus a so-called load leveling has been devised which permits the effective use of generated electric power by storing night power into the secondary batteries installed in general homes to level the load for more efficient utilization. Also, there are increasingly the demand for developing small, lightweight secondary batteries having high energy density for use with the electric automobiles which exhaust no air pollutant, and the demand for developing secondary batteries of high performance for use with the power sources of the portable equipments such as book-type personal computer, word processor, video camera, and portable telephone.

- [0003] As the above-mentioned secondary battery of high performance, a rocking chair type lithium ion battery has been developed in which positive electrode active material has lithium ions introduced into intercalation compound, and negative electrode active material is made of carbon, and partially put to practical use. However, such lithium ion battery has lower energy density than lithium battery which uses metal lithium for the negative electrode active material.

- [0004] The reason why no lithium accumulator of high capacity which uses lithium metal for the negative electrode has not been practically used is considered due to the fact that the occurrence of lithium dendrite (dendritic crystal) which is produced by repetitive charge and discharge and mainly causes short-circuit has not been successfully suppressed. When dendrite of lithium grows to cause a short-circuit between positive and negative electrodes, the energy of battery will be consumed in a short time to produce the heat. The heating will decompose the solvent of electrolyte to produce gases, which increases the inner pressure and eventually may result in some explosion. Also, there is a problem of accident that heating may cause a fire. Accordingly, the development of safe accumulator not bringing about such accident is desired.

- [0005] Also, in the battery involving chemical reaction and having the possibility of firing, the development of safe battery not causing such accident is desired.

- [0006] EP-A-0 486 704 discloses an organic electrolytic battery comprising a negative electrode made of an alkali metal or an alkali metal compound, a positive electrode, and an electrolytic solution, wherein said electrolytic solution comprises a solid organic metal salt consisting of a fluoroalkyl group having at least 4 carbon atoms, an anionic group covalently bonded thereto, and an alkali metal ion or an alkaline earth metal ion ionically bonded to said anionic group.

SUMMARY OF THE INVENTION

- [0007] It is an object of the present invention to resolve the above-mentioned conventional problems and provide a highly safe battery and a secondary battery having high energy density without decreasing battery performance.

- [0008] As a result of careful researches to solve the above conventional problems, the present inventors have found that there is provided a secondary battery with enhanced safety in such a way that the incombustibility of electrolyte is enhanced without decreasing the battery performance by mixing flame retardant such as inert liquid of fluorine compound into electrolyte of battery.

- [0009] The present invention resides in a lithium secondary battery comprising a negative electrode having negative electrode active material, a positive electrode having positive electrode active material with a separator sandwiched between it and said negative electrode active material, and electrolyte solution between said negative electrode and said positive electrode, wherein said electrolyte solution, includes a perfluorocarbon inert liquid as a flame retardant selected from the group consisting of perfluorocarbon compounds of the type C₅F₁₂, C₆F₁₄, C₇F₁₆ and C₈F₁₈, perfluorobutyltetrahydrofuran C₈F₁₆O, perfluorotributylamine (C₄F₉)₃N, perfluorotripropylamine (C₃F₇)₃N, perfluorinated ether, perfluoromethyldecalin and perfluorodecalin.

- [0010] Further, the present invention resides in a lithium secondary battery wherein the surface of the negative electrode having said negative electrode active material opposed to the positive electrode is covered with a membrane capable of transmitting at least lithium ions, and the surface of the positive electrode composed of said positive electrode active material opposed to the negative electrode is covered with a membrane capable of transmitting at least lithium ions.

- [0011] In addition, the present invention resides in a lithium secondary battery wherein said membrane is composed of flame retardant or incombustible material, a lithium secondary battery wherein said negative electrode active material

is lithium or lithium alloy, a lithium secondary battery wherein the mixture ratio by weight of said flame retardant to electrolyte solution is from 1 to 20 wt%, and a lithium secondary battery wherein the boiling point of said perfluorocarbon is 50°C or above.

5 BRIEF DESCRIPTION OF THE DRAWINGS

[0012] Fig. 1 is a typical view showing the basic construction of a lithium secondary battery according to the present invention.

10 [0013] Fig. 2 is a schematic cross-sectional view of a flat lithium secondary battery according to one embodiment of the present invention.

[0014] Fig. 3 is a schematic cross-sectional view of a cylindrical lithium secondary battery according to another embodiment of the present invention.

[0015] Fig. 4 is a graph representing the ion conductivity of electrolyte relative to the additive amount of flame retardant for use in the present invention.

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DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

20 [0016] The present inventors have found, as a result of the examination for a lithium secondary battery formed by adding various kinds of materials to the electrolyte, that the aforementioned problems can be resolved if perfluorine type flame retardant containing fluorine element can meet the following properties:

1. Decomposing no lithium by the reaction with negative electrode having lithium.
2. Not degrading remarkably the ion conductivity of electrolyte.
3. Bringing about as little side reaction as possible except for battery reaction in charging and discharging.
- 25 4. Readily mixed into electrolyte (If mixing is unliable, firing may locally arise).
5. Capability of flame retardancy.

30 [0017] In a lithium secondary battery wherein perfluorine type flame retardant containing fluorine element is added to electrolyte, perfluorine compound which is a flame retardant is thermally decomposed when heating, so that a flame retarding membrane is formed on the lithium surface, and made flame retarding by shutting down oxygen when exposed to external atmosphere. In addition, when using perfluorocarbon, the heat conductivity within the battery can be enhanced, and the local heating at the short-circuit of the battery can be suppressed.

[0018] The relation between the mixing ratio of perfluorine type flame retardant containing fluorine element into the electrolyte and the ion conductivity is as represented in average in Fig. 4.

35 [0019] From Fig. 4, it can be seen that the range of flame retardant added to electrolyte which is capable of enhancing the flame retarding ability without decreasing the ion conductivity is preferably from 1 to 20 wt%, and more preferably from 2 to 10 wt%.

Flame retardant

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[0020] Examples of the flame retardant may include a perfluorine type flame retardant which is particularly effective since perfluorocarbon which is a fluorine compound inert liquid has no influence on electrolytic reaction.

45 [0021] Examples of perfluorocarbon may include C_5F_{12} , C_6F_{14} , C_7F_{16} , C_8F_{18} , perfluorobutyltetrahydrofuran: $C_8F_{16}O$, perfluorotributylamine: $(C_4F_9)_3N$, perfluorotripropylamine: $(C_3F_7)_3N$, perfluorinatedether, perfluoromethyldecalin, and perfluorodecalin. When perfluorocarbon is used by mixing into electrolytic solution (electrolyte), the boiling point is preferably 50°C or greater.

[0022] To maintain the conductivity and the solubility of electrolyte, the mixture ratio of flame retardant into electrolytic solution is preferably from 1 to 20 wt%, and more preferably from 2 to 10 wt%.

50 (Constitution of battery according to the first invention of this application)

55 [0023] The basic constitution of a secondary battery according to the present invention is comprised of a negative electrode (101) at least composed of negative electrode active material, a separator (108), a positive electrode (103) at least composed of positive electrode active material, electrolyte selected from perfluorine type flame retardant containing fluorine element, and a collector. Fig. 1 shows a basic constitutional view of the secondary battery according to the present invention. In Fig. 1, 101 is a negative electrode composed of negative electrode active material, 102 is a negative electrode collector, 103 is a positive electrode composed of positive electrode active material, 104 is a positive electrode collector, 105 is an electrolytic solution (electrolyte) containing flame retardant, 106 is a negative

electrode terminal, 107 is a positive electrode terminal, 108 is a separator, and 109 is a battery case.

[0024] In a lithium battery in which the negative electrode active material of negative electrode 101 is lithium or lithium alloy, lithium ions (not shown) in electrolyte 105 enter the intercalation of positive electrode active material of positive electrode 103, with discharge reaction, while dissolving into electrolyte 105 from the negative electrode active material. On the other hand, with charge reaction, lithium ions in electrolyte 105 pass through separator 106 to be deposited as lithium metal on the negative electrode active material (wherein dendrite is likely to grow), while lithium of the intercalation for the positive electrode active material 103 of positive electrode dissolves into the electrolyte 105, and if dendrites grow from the negative electrode, penetrates through the separator, ultimately resulting in the short-circuit between positive electrode and negative electrode, which causes the energy to be consumed in short time to bring about firing in some instances. Because the electrolytic solution 105 contains flame retardant selected from perfluorine type flame retardant containing fluorine element, organic solvent which is a solvent for the electrolytic solution can be rendered flame retarding even if it is flammable, so that firing can be suppressed. Therefore, the selectivity of solvent material for the electrolytic solution can be improved.

Collector

[0025] Examples of collector material usable may include electrically conductive materials such as carbon, stainless steel, titanium, nickel, copper, platinum, and gold.

[0026] The shape of collector may be any shape of fiber, pore, or mesh.

(Positive electrode)

[0027] Positive electrode is formed by mixing positive electrode active material, conducting material powder and binding agent, and adding solvent, as required, and molding with collector.

Positive electrode active material

[0028] Examples of the positive electrode active material for use, the intercalation of which lithium enters, may include metal oxides such as nickel oxide, cobalt oxide, titanium oxide, iron oxide, vanadium oxide, manganese oxide, molybdenum oxide, chromium oxide, and tungsten oxide, metal sulfides such as molybdenum sulfide, iron sulfide and titanium sulfide, hydroxides such as iron oxyhydroxide, and conducting polymers such as polyacetylene, polyaniline, polypyrrole, and polythiophene.

[0029] Herein, examples of the transition metal element for the transition metal oxides or transition metal sulfides may include elements partially having d shell or f shell, such as Sc, Y, lanthanoid, actinoid, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, and Au. Mainly, the first transition series metals are used, such as Ti, V, Cr, Mn, Fe, Co, Ni, and Cu.

Conductive substance powder

[0030] The role of conductive substance powder is to assist in electron conduction and facilitate current collection when the active material has poor conductivity.

[0031] Examples of conductive substance powder may include a variety of carbon materials such as acetylene black, ketchen black, graphite powder, and metal materials such as nickel, titanium, copper, and stainless steel. The mixture weight ratio of conductive substance powder to active material is preferably 1 or less.

Binding agent

[0032] Binding agent has a role of binding together active material powders to prevent cracks from occurring and falling off the collector in the charge and discharge cycle, when the moldability of active material is bad. Examples of the binding agent material may include fluororesin, polyethylene, polypropylene, and silicone resin, which are stable in the solvent. The above resins should be liquid or solution, or have a lower melting point, because the content of binding agent in the electrode can be lowered without decreasing the battery capacity. Specific examples of the resin liquid or dissolvable in the solvent may include, in addition to polyethylene and polypropylene, fluororesin and silicone resin containing ether bond. In particular, when fluororesin having ether bond is used, it can be dissolved in solvent for use at lower concentration, so that the content in the positive electrode can be decreased and the porosity can be raised.

Negative electrode active material

[0033] Examples of the negative electrode active material may include lithium and lithium alloy. Examples of lithium alloy may include the alloys of magnesium, aluminum, potassium, sodium, calcium, zinc and lead with lithium.

Separator

[0034] Separator has a role of preventing the short-circuit between negative and positive electrodes. Also, it may have a role of holding electrolytic solution. Separator has fine pores through which ions involved in battery reaction are movable, and is required to be insoluble in the electrolytic solution and stable, and may be a nonwoven fabric made of glass, polypropylene, polyethylene, or fluororesin, or a material of microporous structure. Also, a metal oxide film having fine pores or a resin film having metal oxide compound may be used. In particular, when a metal oxide film having multilayer structure is used, there is the effect of preventing any short-circuit because dendrite is unlikely to pass therethrough. When a fluororesin film which is a flame retardant or a glass or metal oxide film which is an incombustible material is used, the stability can be enhanced.

Electrolyte

[0035] Electrolyte is used in the state as it is, or in the state of solution dissolved in solvent, or in the stiffened state by adding a gelatinizer such as polymer to the solution. Normally, electrolyte is used by retaining electrolytic solution having electrolyte dissolved in solvent in a porous separator.

[0036] The conductivity of electrolyte or electrolytic solution is preferred to be higher. The conductivity at least at 25°C is desirably 1×10^{-3} S/cm or more, and more preferably 5×10^{-3} S/cm or more.

[0037] Examples of the electrolyte may include salts composed of lithium ion (Li^+) and Lewis acid ion (BF_4^- , PF_6^- , AsF_6^- , ClO_4^-), and mixture salts thereof. In addition to the above support electrolytes, salts of cation such as sodium ion, potassium ion, tetraalkylammonium ion with Lewis acid ion may be used. The above salts are desirably dewatered and deoxidized by heating under lower pressure.

[0038] Examples of the solvent for electrolyte may include acetonitrile, benzonitrile, propylene carbonate, ethylene carbonate, dimethylformamide, tetrahydrofuran, nitrobenzene, dichloroethane, diethoxyethane, chlorobenzene, γ -butyrolactone, dioxolane, sulfolane, nitromethane, dimethylsulfide, dimethylsulfoxide, dimethoxyethane, methyl formate, 3-methyl-2-oxazolidinone, 2-methyltetrahydrofuran, sulfur dioxide, phosphoryl chloride, thionyl chloride, sulfuryl chloride, and mixture solutions thereof.

[0039] The above solvents are dewatered by activated alumina, molecular sieve, phosphorus pentoxide, or calcium chloride, or may be distilled in inert gas atmosphere under the coexistence of alkaline metal to effect the removal of impurities and dewatering, depending on the solvent.

[0040] To prevent any leakage of electrolytic solution, the gelatinization is desirable. Gelatinizer is desirably a polymer which swells by absorbing the solvent of electrolytic solution, examples of which may include polyethylene oxide, polyvinyl alcohol, and polyacrylamide.

(Negative electrode or positive electrode covering)

[0041] When the negative electrode active material is lithium, there may occur dendrite which causes a short-circuit at the time of charging, and to prevent the occurrence of such dendrite, negative electrode or positive electrode or the surface of negative electrode and positive electrode should be covered with a membrane through which lithium ions can pass to elongate the cycle life of battery.

[0042] Examples of covering material may include polymers of macrocyclic compound derivative, polymers of aromatic hydrocarbon derivative, fluororesin, silicone resin, titanium resin, polyolefin, or inorganic oxides, nitrides, carbides and halogenides. The covering of fluororesin, polyphosphazene, inorganic oxide, nitride, carbide and halogenide with flame retardant or incombustible material is effective to further enhance the safety of lithium secondary battery.

(Shape and structure of battery)

[0043] The practical shape of battery may be flat, cylindrical, rectangular or sheet-like. The spiral cylindrical type can have a larger electrode area by winding the electrode with a separator sandwiched between positive and negative electrodes to allow a larger electric current to flow in charging and discharging. Also, the rectangular type allows the effective use of storage space for the equipment where battery is stored. The structure may be of the single layer or multi-layer type.

[0044] Figs. 2 and 3 illustrate schematic cross-sectional views of a single layer type flat battery and a spiral structure

cylindrical battery. In Figs. 2 and 3, 201 and 301 are negative electrodes made of negative electrode active material, 202 and 302 are negative electrode collectors, 203 and 303 are positive electrodes made of positive electrode active material, 304 is a positive electrode collector, 206 and 306 are negative electrode terminals (negative electrode caps), 207 and 307 are outer packaging cans (positive electrode cans) which are also used as the battery case, 208 and 308 are separators holding the electrolytic solution containing flame retardant, 210 and 310 are insulating packings, and 311 is an insulating plate.

[0045] An example of assembling the battery of Figs. 2 and 3 involves incorporating a positive electrode 203, 303 and a negative electrode 201, 301, with a separator 208, 308 sandwiched therebetween, into a positive electrode can 207, 307, injecting the electrolytic solution containing flame retardant, placing a negative cap 206, 306 and an insulating packing 210, 310, and caulking to fabricate the battery.

[0046] It should be noted that the preparation of lithium battery material and the assembling of battery are desirably made in the dry air with water contents removed sufficiently, or in the dry inert gas.

Battery case (outer packaging can)

[0047] Battery case may be a metallic outer packaging case which is also used as the output terminal, or a plastic resin case.

[0048] Examples of the material for positive electrode can 207, 307 or negative cap 206, 306 of actual battery may include stainless steel, in particular, titanium clad stainless, copper clad stainless, and nickel plated steel plate.

[0049] In Figs. 2 and 3, the positive electrode can 207, 307 is also used as the battery case, examples of the material of which may include, in addition to stainless steel, metals such as aluminum, plastics such as polypropylene, or composites of metal or glass fiber with plastics.

Insulating packing

[0050] Examples of the material for insulating packing 210, 310 may include fluororesin, polyamide resin, polysulfone resin, and a variety of rubbers.

Sealing

[0051] The sealing may be made by adhesive, welding, soldering, glass sealing, in addition to caulking using a gasket such as insulating packing.

Insulating plate

[0052] The material of insulating plate usable for the insulation or isolation within the battery may be any of a variety of organic resins, or ceramics.

Safety valve

[0053] The safety measure against increased inner pressure of battery, not shown in Figs. 2 and 3, involves providing a safety valve using rubber, spring, or metallic hole.

(Battery safety evaluation)

[0054] The safety evaluation tests for the battery are as follows.

Short-circuit test

[0055] Confirmation test as to whether or not firing occurs when the battery temperature rises by short-circuiting the positive electrode and the negative electrode via copper wire after charging at 25°C and 85°C.

Nailing test

[0056] Confirmation test as to whether or not firing or explosion occurs when the battery temperature rises by penetrating a nail having a diameter of 3 millimeters into the charged battery.

Burning test

[0057] Confirmation test to ensure that no furious burning occurs by throwing a charged battery into carbide.

5 Water immersion test

[0058] Confirmation test to ensure that no burst or explosion occurs by immersing in city water having a temperature of 25°C for fourteen days.

10 High temperature storage test

[0059] Confirmation test to ensure that the battery temperature is not more than 130°C and there is no fuming, explosion and firing by storing a battery at 100°C for five hours.

15 Overcharge

[0060] Confirmation test to ensure that no firing occurs even if the battery temperature rises by charging for a rate of 10 hours with a terminal voltage of 5.0 volts, and for 24 hours with the cut-off.

[0061] The present invention will be described in detail based on the examples. It should be noted that the present invention is not limited to such examples.

(Example 1)

[0062] A lithium secondary battery of a schematic cross-sectional structure as shown in Fig. 3 was fabricated.

25 [0063] As the positive electrode active material, lithium manganese oxide was prepared by mixing electrolyzed manganese dioxide and lithium carbonate at a ratio of 1 to 0.4, and then heating at 800°C. After mixing graphite and powder fluororesin paint Superconac (made by Nippon Oil & Fats) to prepared lithium manganese oxide, the mixture was molded under pressure to nickel mesh 304, and subjected to thermal treatment at 170°C to form a positive electrode 303.

30 [0064] A titanium mesh collector with lead 302 was connected under pressure from the back side to a lithium metal foil in the dry argon gas atmosphere, and covered with a fluororesin paint Lumifron thin film (made by Asahi Glass) to prepare a lithium negative electrode 301. The electrolytic solution was prepared by dissolving borate tetrafluoride lithium salt into an equivalent mixture solvent of propylene carbonate (PC) and dimethoxyethane (DME) and mixing a fluorine type inert liquid by 10 wt% thereto.

35 [0065] Separator 308 was composed of an alumina film, a polypropylene non-woven fabric, and a microporous separator of polypropylene which were bonded together.

[0066] The assembling was performed in such a way as to sandwich a separator 308 between negative electrode 301 and positive electrode 303, then rolling and inserting the entirety into a positive electrode can 307 made of stainless material of titanium clad, connecting a collector lead, injecting electrolytic solution, and enclosing the whole structure by a negative electrode cap 306 with safety valve made of stainless material of titanium clad and an insulation packing 40 310 made of fluorine rubber to fabricate a spiral cylindrical lithium secondary battery.

(Comparative example 1)

45 [0067] A lithium secondary battery was fabricated in the same way as in example 1, with the exception that aluminum hydroxide as flame retardant was mixed by 10 wt% to electrolytic solution, instead of fluorine type inert liquid in example 1.

(Evaluation of flame resistance)

50 [0068] A portion consisting of the negative electrode, the separator holding flame retardant and electrolytic solution, and the positive electrode bonded together in the lithium secondary battery in the example 1 was taken out, and cut out 30.48cm (12 inches) in length to have a test sample piece. Fisher Body Match Test as set forth below was conducted and confirmed that test sample of example 1 was self-extinguishing (note that in Fisher Body Match Test, a flame of match was subjected for 15±5 seconds to a test sample 30.48 cm (12 inches) long which was stood vertically, and 55 judged to be self-extinguishing when not burning more than 15.24 cm (6 inches) and flammable when burning 15.24 cm (6 inches) or greater).

[0069] To further enhance the effect of flame retardant, a test sample piece for flame resistance evaluation, which

was equivalent except that no flame retardant was added in the example 1 was prepared for the comparison test, and Fisher Body Match Test was conducted. The result was such that since the separator made of polypropylene holding electrolytic solution was burnt, the test piece was judged flammable. Also, in the example 1 a test sample piece for the comparison was fabricated in the same way, except that no flame retardant was added and the surface of negative electrode was not covered. This test sample piece was subjected to Fisher Body Match Test and judged flammable because lithium negative electrode was also burnt, besides the polypropylene separator holding electrolytic solution. [0070] From the above evaluation of flame resistance, it could be found that the safety against firing was improved with the present invention.

(Safety evaluation for lithium secondary battery)

[0071] For the lithium secondary battery fabricated in the example 1 charge and discharge was repeated by 20 cycles, and after charging, the safety was evaluated in accordance with the following test method. Excellent test results could be obtained for the lithium secondary battery.

Short-circuit test

[0072] It was confirmed that no firing occurred when the battery temperature rose by short-circuiting the positive electrode and the negative electrode via a copper wire after charging at 25°C and 85°C.

Nailing test

[0073] It was confirmed that no firing or explosion occurred when the battery temperature rose by penetrating a nail having a diameter of 3 millimeters into charged battery.

Burning test

[0074] It was confirmed that no furious burning occurred by throwing a charged battery into carbide.

Water immersion test

[0075] It was confirmed that no firing or explosion occurred by immersing in city water at a temperature of 25°C for fourteen days.

Overcharge

[0076] It was confirmed that no firing occurred even if the battery temperature rose by charging for a rate of 10 hours at a terminal voltage of 5.0 volts, and for 24 hours at the cut-off.

[0077] From the results of safety evaluation test as above described, it has been found that the lithium secondary battery of the present invention has high safety even after the repetition of charge and discharge, despite the use of metal lithium for the negative electrode active material.

[0078] Also, the same test was conducted for the comparative example 1, so that substantially the equivalent results were obtained, but the significant difference was seen in the battery performance.

(Performance test for battery)

[0079] The self-discharge rate calculated from the discharge capacity at the first cycle and the discharge capacity one month after charging was obtained for the example 1 and the comparative example 1, and the performance of example was compared when the performance of comparative example was supposed 1.

[0080] The results are listed in Table 1. From the relative comparison between example 1 and comparative example 1 it can be found that the battery performance degrades when aluminum hydroxide is used as the flame retardant.

Table 1

| | Discharge capacity | Self-discharge rate |
|--|--------------------|---------------------|
| Example 1/ Comparative example 1 | 1.4 | 0.1 |

Claims

1. A lithium secondary battery comprising a negative electrode having negative electrode active material, a positive electrode having positive electrode active material, a separator sandwiched between said negative electrode and said positive electrode, and an electrolyte solution between said negative electrode and said positive electrode, wherein said electrolyte solution includes a perfluorocarbon inert liquid as a flame retardant selected from the group consisting of perfluorocarbon compounds of the type C_5F_{12} , C_6F_{14} , C_7F_{16} and C_8F_{18} , perfluorobutyltetrahydrofuran $C_8F_{16}O$, perfluorotributylamine $(C_4F_9)_3N$, perfluorotripropylamine $(C_3F_7)_3N$, perfluorinated ether, perfluoromethyldecalin and perfluorodecalin.
2. A lithium secondary battery according to claim 1, characterized in that the surface of said negative electrode opposed to the positive electrode is covered with a membrane capable of transmitting at least lithium ions.
3. A lithium secondary battery according to claim 1, characterized in that the surface of said positive electrode opposed to the negative electrode is covered with a membrane capable of transmitting at least lithium ions.
4. A lithium secondary battery according to claim 2, characterized in that said membrane is made of flame retardant or incombustible material.
5. A lithium secondary battery according to claim 1, characterized in that said negative electrode active material is lithium or lithium alloy.
6. A lithium secondary battery according to claim 1, characterized in that the mixture ratio by weight of perfluorocarbon in electrolyte solution is from 1 to 20 wt. %.
7. A lithium secondary battery according to claim 1, characterized in that the boiling point of said perfluorocarbon is 50 °C or above.
8. A lithium secondary battery according to claim 3, characterized in that said membrane is made of a flame retarding material or an incombustible material.

Patentansprüche

1. Lithiumsekundärbatterie, die eine negative Elektrode mit einem aktiven Material der negativen Elektrode, eine positive Elektrode mit einem aktiven Material der positiven Elektrode, eine Trenneinrichtung, die zwischen der negativen Elektrode und der positiven Elektrode liegt und eine Elektrolytlösung zwischen der negativen Elektrode und der positiven Elektrode umfasst, wobei die Elektrolytlösung eine inerte Flüssigkeit aus einem Perfluorkohlenwasserstoff als ein flammhemmendes Mittel einschließt, die aus der Gruppe ausgewählt ist, die aus Perfluorkohlenwasserstoffverbindungen des Typs C_5F_{12} , C_6F_{14} , C_7F_{16} und C_8F_{18} , Perfluorbutyltetrahydrofuran $C_8F_{16}O$, Perfluortributylamin $(C_4F_9)_3N$, Perfluortripropylamin $(C_3F_7)_3N$, perfluoriertem Ether, Perfluormethyldecalin und Perfluorodecalin besteht.
2. Lithiumsekundärbatterie gemäß Anspruch 1, dadurch gekennzeichnet, dass die Oberfläche der negativen Elektrode, die der positiven Elektrode gegenüber liegt, mit einer Membran bedeckt ist, die wenigstens für Lithiumionen

durchlässig ist.

3. Lithiumsekundärbatterie gemäß Anspruch 1, dadurch gekennzeichnet, dass die Oberfläche der positiven Elektrode, die der negativen Elektrode gegenüber liegt, mit einer Membran bedeckt ist, die wenigstens für Lithiumionen durchlässig ist.
4. Lithiumsekundärbatterie gemäß Anspruch 2, dadurch gekennzeichnet, dass die Membran aus einem flammhemmenden Mittel oder einem unbrennbaren Material aufgebaut ist.
5. Lithiumsekundärbatterie gemäß Anspruch 1, dadurch gekennzeichnet, dass das aktive Material der negativen Elektrode Lithium oder eine Lithiumlegierung ist.
6. Lithiumsekundärbatterie gemäß Anspruch 1, dadurch gekennzeichnet, dass das massebezogene Mischungsverhältnis des Perfluorkohlenwasserstoffes in der Elektrolytlösung zwischen 1 und 20 Masse-% liegt.
7. Lithiumsekundärbatterie gemäß Anspruch 1, dadurch gekennzeichnet, dass der Siedepunkt des Perfluorkohlenwasserstoffes bei 50 °C oder darüber liegt.
8. Lithiumsekundärbatterie gemäß Anspruch 3, dadurch gekennzeichnet, dass die Membran aus einem flammhemmenden Mittel oder einem unbrennbaren Material aufgebaut ist.

Revendications

1. Batterie secondaire au lithium comprenant une électrode négative ayant une matière active en tant qu'électrode négative, une électrode positive ayant une matière active en tant qu'électrode positive, un séparateur pris en sandwich entre ladite électrode négative et ladite électrode positive, et une solution d'électrolyte entre ladite électrode négative et ladite électrode positive, dans laquelle ladite solution d'électrolyte comprend un liquide inerte perfluorocarboné en tant qu'agent retardateur de flamme choisi dans l'ensemble constitué par des composés perfluorocarbonés de type C_5F_{12} , C_6F_{14} , C_7F_{16} et C_8F_{18} , le perfluorobutyltétrahydrofuranne $C_8F_{16}O$, la perfluorotributylamine $(C_4F_9)_3N$, la perfluorotripropylamine $(C_3F_7)_3N$, un éther perfluoré, la perfluorométhyldecaline et la perfluorodécaline.
2. Batterie secondaire au lithium selon la revendication 1, caractérisée en ce que la surface de ladite électrode négative opposée à l'électrode positive est recouverte d'une membrane capable de transmettre au moins des ions lithium.
3. Batterie secondaire au lithium selon la revendication 1, caractérisée en ce que la surface de ladite électrode positive opposée à l'électrode négative est recouverte d'une membrane capable de transmettre au moins des ions lithium.
4. Batterie secondaire au lithium selon la revendication 2, caractérisée en ce que ladite membrane est formée d'un agent retardateur de flamme ou d'une matière incombustible.
5. Batterie secondaire au lithium selon la revendication 1, caractérisée en ce que ladite matière active en tant qu'électrode négative est du lithium ou un alliage de lithium.
6. Batterie secondaire au lithium selon la revendication 1, caractérisée en ce que le pourcentage en poids de mélange de perfluorocarbonate dans la solution d'électrolyte est de 1 à 20 % en poids.
7. Batterie secondaire au lithium selon la revendication 1, caractérisée en ce que le point d'ébullition dudit perfluorocarbonate est de 50°C ou plus.
8. Batterie secondaire au lithium selon la revendication 3, caractérisée en ce que ladite membrane est formée d'une matière retardatrice de flamme ou d'une matière incombustible.

FIG. 1

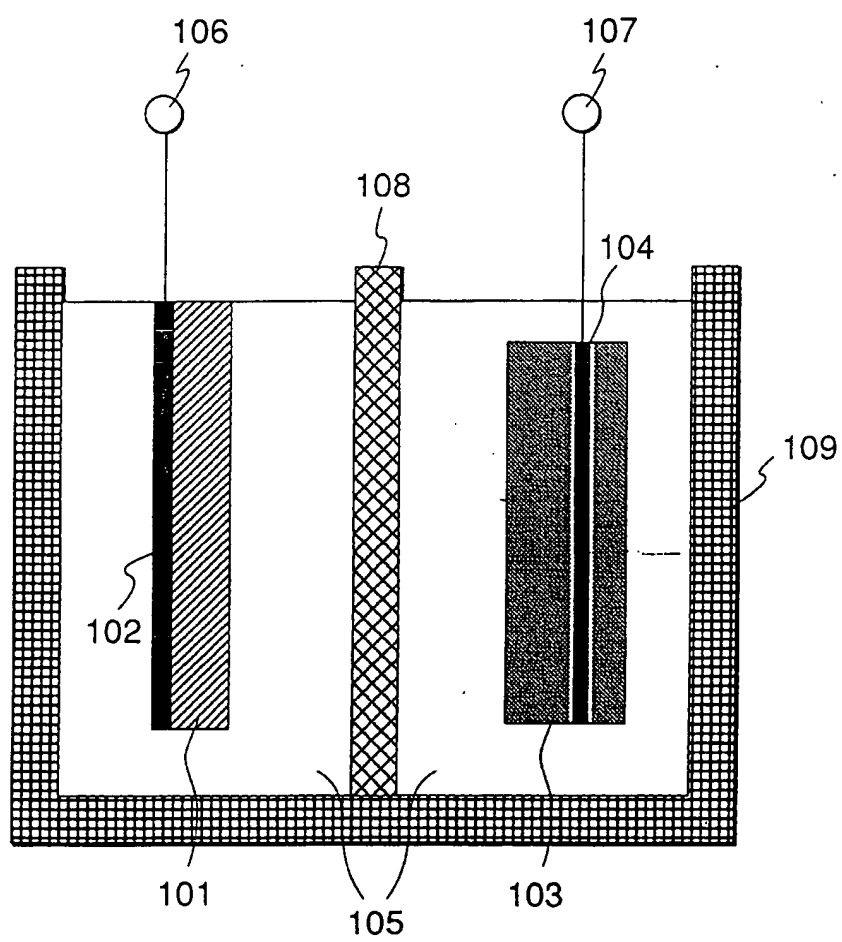


FIG. 2

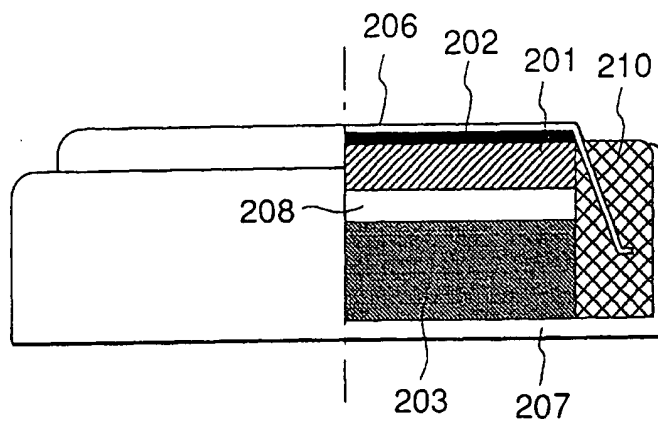


FIG. 3

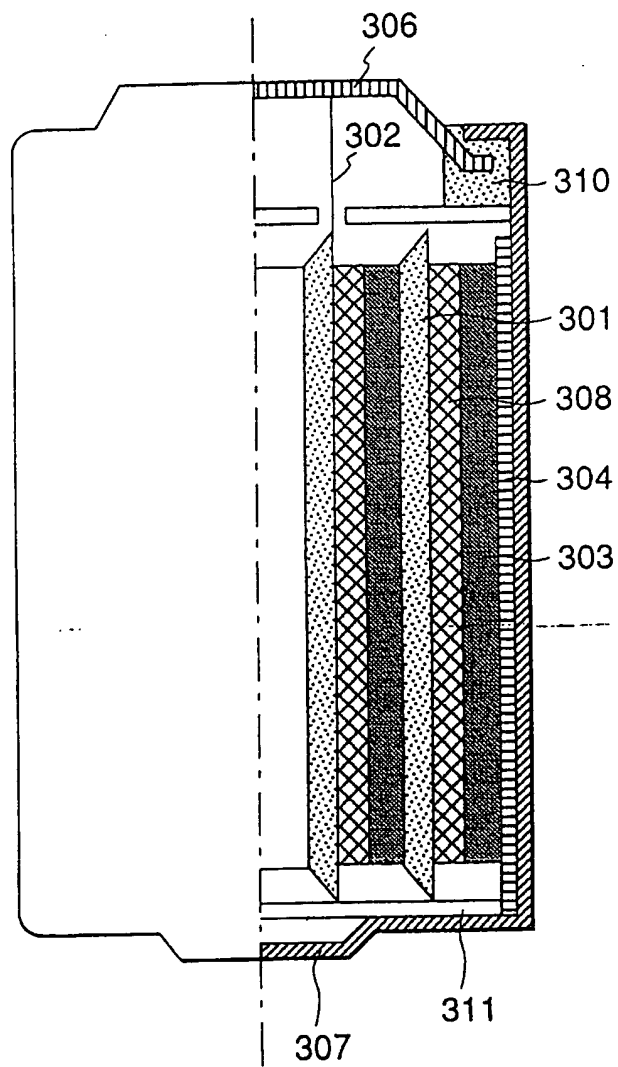


FIG. 4

